Invited article

Environmental application and ecological significance of nano-zero valent iron

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ABSTRACT

Toxicity studies considering both the bare and stabilized forms of zero valent iron nanoparticles (nZVI) could be timely, given that ecological risks identified are minimized through modification or with substitution of approaches in the synthesis, development and environmental application of the nanoparticles before succeeding to volume production. This review is focused on the fate, transport and toxicological implications of the bare nZVI and surface modified particles used for environmental applications.

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Introduction

By virtue of the large surface-to-volume ratio and an increase in proportion of surface and near surface atoms, engineered nanoparticles (eNPs) exhibit unique mechanical, optical, electronic and magnetic properties with promising benefits for a wide variety of environmental applications (Zhang, 1997, 2003; Kamat and Meisel, 2003; Li et al., 2006; Wiek et al., 2009; Serrano et al., 2009; Crane and Scott, 2012). These particles have rapid chemical reactivity with a considerably long reactive life span and mobility within porous media. These properties have led them to the selection for onsite environmental remediation (Macé et al., 2006) and are the rationale for extensive research on their application (Zhang, 1997; Li et al., 2006).

Compared to their colloidal forms, the use of eNPs provides application flexibility in terms of their use for both in-situ and ex-situ environmental remediation (Burton, 2009; Karn et al., 2009; Zhang, 2003). In the case of groundwater remediation, nanoparticles are generally applied through application wells where the particles migrate and induce oxidation–reduction (redox) reactions with contaminants. This technology is cost-effective and mostly assumed to be environmentally friendly compared to traditional methods of treatment. For example, due to the small size, they can be injected to geologic matrix far where microbes even are not available to degrade.

One of the examples of such application is the use of zero valent iron nanoparticles (nZVI) due to their versatile ability for contaminant remediation and an assumption that they are less toxic and bioavailable (Greenlee et al., 2012; Crane and Scott, 2012). The nZVI, emerged as an extension of the micro-scale zero-valent iron technology, is a critical component in reduction–oxidation (redox) processes with a

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characteristic role of enhancing reactivity (Greenlee et al., 2012). It is the most widely studied and used for field application, holding great promise for environmental remediation of various organic and inorganic contaminants through oxidation and reduction reactions (Li et al., 2008). This review summarizes the advances and environmental applications of nZVI technologies. The last section in this chapter presents discussions on the toxicity of various forms of nZVI to ecologically important organisms.

1. Synthesis and performance of nZVI

1.1. Synthesis of nZVI

Approaches used in the fabrication of nZVI are: the top-down approach which starts the use of bulk material of the particle and the bottom-up approach which builds the nZVI particles with the use of atom-by-atom or molecule-by-molecule approaches. The chemical synthesis using an iron salt and sodium borohydride (Eq. (1)) is a commonly used method due to the easiness in synthesis which requires only a simple lab set-up for the production of highly reactive nZVI. Particles synthesized using chemical approach is nearly polydispersed in size. In addition, the production of hydrogen gas is a safety concern during the synthesis which requires safe handling and use of explosion-resistant mixers.

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0\downarrow + 3H_2BO_3^- + 12H^+ + 6H_2\uparrow \qquad (1)$$
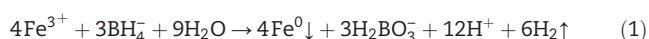
1.2. Characteristic properties of nZVI

The structural properties of nZVI such as size and surface area may vary depending on the synthesis conditions. Bare forms of nZVI particles have dimensions less than 100 nm, typically within a range of 10 to 100 nm where the form of nZVI mostly comprises of spherical iron. The smaller the particle size, the higher the surface area to volume ratio will be, resulting in higher surface reactivity (Fig. 1). For example, in the report by Wang and Zhang (1997), the micro size iron powder with a particle size of <10 μm had the surface area to mass ratio of <1 m^2/g, whereas for the synthesized nano-size iron particle (<100 nm), the surface area to mass ratio was 33.5 m^2/g. Moreover, relative to the total number of atoms of the particle, greater proportion of atoms or molecules with unsatisfied valence tends to be at the surface of the particle, whereas for the micro size ZVI, the proportion of atoms at the surface is minuscule (Nel et al., 2006). These surface atoms are an important implication for particles to adsorb or react with other atoms to attain surface stabilization.

Practically unavoidable phenomena during the synthesis process of nZVI or following its reaction with water or air are the rapid changes in surface property, thereby develop core-shell morphology. The shell composition could further affect the size, size distribution, degree of crystallinity, reactivity and aging of the particle (Fig. 2). The spontaneous formation of a thin layer of iron (oxy)hydroxide (Ramos et al., 2009) and magnetite (Liu et al., 2005; Phenrat et al., 2006; Nurmi et al., 2004) shell during synthesis with varying surface

reactivity and remedial efficiency was reported. This structure is central to the property of nZVI in remediation as the oxide layer allows electron transfer for reducing contaminant while the core-shell facilitates efficient adsorption of various contaminants due to the electrostatic interactions and surface complexation (Yan et al., 2010; O'Carroll et al., 2013). In addition, shell is protective of rapid oxidation of the ZVI core due to the insoluble species of iron oxides under neutral pH conditions.

1.3. Factors affecting performance of nZVI

Iron nanoparticles have been used as a permeable reactive barrier-a barrier few meters wide-for the past two decades. Application was demonstrated at laboratory and field scale to remediate contaminants including nitrates, bromates, chlorates, nitroaromatic compounds, chlorinated organic compounds, pesticides, arsenic, lead, and hexavalent chromium. Although reactivity of nZVI is affected by the size of the particles, their performance could be affected by factors such as geochemical processes, passivation, and agglomeration.

1.3.1. Geochemical process
Fe(0) is an excellent source of reducing equivalents-serving as original source of electron donor such as Fe^{+2} or H$_2$ (Eq. (2)).

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (\Delta G^\circ = -5.0 \text{ kJ}; \ E^\circ = 0.440 \text{ V}) \qquad (2)$$
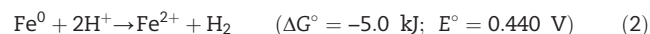
where, ΔG° and E° stand for Gibbs free energy and reduction potential, respectively. However, in geochemical processes (such as reaction with chemicals in soil or water), the available reducing equivalents of nZVI for reaction with the target contaminants will reduce (O'Carroll et al., 2013). Characteristic behavior of nZVI and their performance in remediation may vary depending on the composition of the soil matrix, ionic strength of the groundwater, and geochemical properties such as pH, dissolved oxygen, oxidation reduction potential (ORP) (Liu and Lowry, 2006). Thus, for better performance of nZVI, comprehensive understanding of the geologic and hydrogeologic conditions should be essential before nZVI are injected.
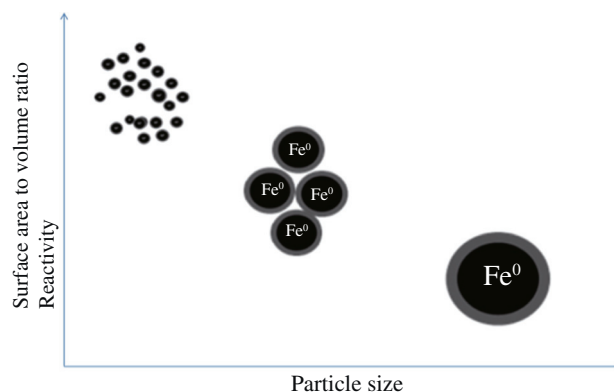

Fig. 1 – Relationship between surface area, reactivity and particle size.

1.3.2. Passivation effect

In practical application, nZVI are exposed to corrosion whereby the iron surface would be coated by corrosion products and other precipitates such as iron (III) hydroxides, goethite, hematite, lepidocrocite and maghemite. The use of a volume of water injected along with the iron is limiting as the exposure of nZVI to oxygen and other oxidants causes passivation (*i.e.*, the loss of redox reactivity) through the limit in electron transfer and hydrogen formation reactions. Passivation as a consequence results in a reduction in rate of treating targeted contaminants. On the other hand, the formation of mixed valent iron oxides, such as magnetite, can promote remediation reaction (Chien et al., 2005).

1.3.3. Agglomeration

As shown in Fig. 2, another limitation is that nZVI has limited mobility in water saturated porous media as a consequence of aggregation and attachment to or deposition on aquifer materials (Phenrat et al., 2006). This could be due to the physical nature of the particle such as size and zeta (ζ) potential, application concentration, and Brownian motion (Phenrat et al., 2006, 2009a). Random collision of particles in the environmental system is constant as a result of Brownian motion, and when the energy of affinity for the surfaces of soil grains exceeds the energy of repulsion, agglomeration will occur (Tourinho et al., 2012). Here in this review, the terms agglomerate and aggregate are used interchangeably as stated in reports, otherwise it's mentioned with no regard to the strength of attachment of particles but simply to mention the clump of particles. Studies have found a limit in the radius of influence of nZVI when applied into the soil or groundwater matrix, due to the agglomeration before they completely disperse (Johnson et al., 2013). The nZVI particles with high zeta potential values, *i.e.*, greater than +30 mV and less than −30 mV are stable; otherwise, nZVI particles will have the maximum instability at the zeta potential of zero where the particles tend to aggregate due to the Van der Waals force overcoming electrostatic repulsion. Notably, under environmental conditions, aggregation of particles could possibly affect mobility, interfacial free energy, environmental behavior, reactivity, toxicity or biological activity, and cause risk to the environment. Additionally, because of the agglomeration, the actual size of the particles may appear as hundreds of nanometers. Hence, a renewed approach to enhance its stability has been proposed through surface modification of nZVI using physical and chemical functionalization

Fig. 2 – Environmental behavior of bare and stabilized zero valent iron nanoparticles (nZVI).

techniques (Krajangpan et al., 2012; Krol et al., 2013; Wei and Wu, 2010; Long and Ramsburg, 2011; Wei et al., 2012).

1.4. Stabilization of nZVI

Approaches such as support of the nZVI particles onto granular particles and/or modifying the nZVI surface are used to stabilize the particle against aggregation. This protection is due to the electrosteric repulsive forces which are subject to surface concentration and charge density of the adsorbed polyelectrolyte layer (Phenrat et al., 2008b). Reactivity of the surface of nZVI particle could be modified via reducing access to reactive sites. For example, experimental study was carried out examining the effect of adsorbed polyelectrolyte on reactivity of nZVI as a function of trichloroethene (TCE) dechlorination (Phenrat et al., 2009b). The study revealed a significant decrease in dechlorination rate constant while reaction pathways were not affected. The study suggested the possibility of the adsorbed polyelectrolyte to block reactive sites of the nZVI surface.

Generally, stabilization of nZVI using various polyelectrolyte, such as poly acrylic acid (PAA) (Yang et al., 2007; Li et al., 2006; Lin et al., 2010), polyaspartate (PAP), surfactants (Saleh et al., 2008), carboxymethyl cellulose (CMC) (Lin et al., 2010) and starch (He and Zhao, 2005), is commonly employed, and the mobility (migration) and therefore the proximity to the pollutant materials and life time will be higher (Fig. 2) (Kim et al., 2009; Phenrat et al., 2006; Saleh et al., 2005, 2008). This enhanced mobility through direct application to groundwater, such as mobility for eight months (Kim et al., 2009), increases the possibility that surface-supported nZVI could enter aquifers and may have the chance of impacting biological systems. Fig. 3 shows the stabilization of nZVI using poly acrylic acid (PAA).

1.5. Environmental application

Since the early 1990s, zero valent iron (ZVI) or elemental iron (Fe⁰) has been developed as a cost-effective technology for the remediation of environmental contaminants (Gillham and O'Hannesin, 1994; Comba et al., 2011). Currently, the nano-scale ZVI has emerged as a new technology which could be used as advancement for the granular form of ZVI with the goal of improving the remediation efficiency via reduction of contaminant mass and flux across the down gradient. The use of nZVI is a promising option for the treatment of source zones (Taghavy et al., 2010).

Effective in-situ remediation involves introduction of nZVI into a system (3–10 m soil depth) through proper handling and injection of concentrations of slurry (nZVI powder and water). This application requires careful preparation through prevention of slurry preparation from surface passivation which may affect reactivity and mobility of nZVI particles. Passivation can be reduced by limiting the amount of aerated water used in the preparation of slurry causing the nZVI particles the ability to migrate efficiently through media and reach a contaminant source zone, particularly areas of a challenge to other treatment methods (Nyer and Vance, 2001; Zheng et al., 2008; Ponder et al., 2000b; Zhang, 2003). Several ranges of slurry concentrations, such as 0.75 to 50 g/L (Henn
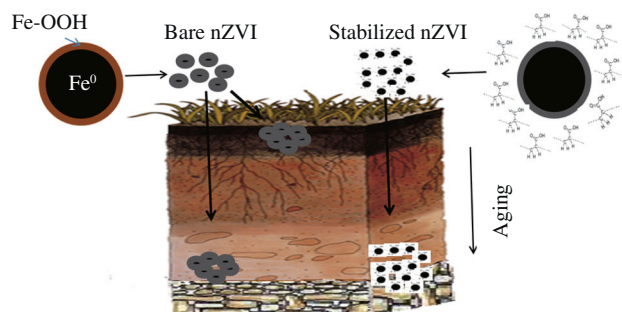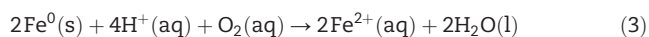
and Waddill, 2006; Mueller et al., 2012), have been trialed depending on the geophysical nature, nature of contaminant, concentration and plume dimension. NZVI is the reactive reagent, and applications in vadose-zone soil or shallow groundwater rapidly oxidize nZVI to ferrous (Fe^{2+}), as shown below, and ferric iron (Fe^{3+}) leading the released electron to become available for the reduction of other compounds, whereas, through Fenton chemistry (Eqs. (3) and (4)), which produces strong oxidants capable of transforming recalcitrant environmental contaminants such as chlorinated compounds, pesticides, polychlorinated biphenyls, inorganic anions and heavy metals (Keenan and Sedlak, 2008; Joo et al., 2004; Kanel et al., 2005). NZVI exposed to environmental conditions will be oxidized under both oxic and anoxic conditions (Mylon et al., 2010; Tanboonchuy et al., 2011; Shin and Cha, 2008).

$$2Fe^0(s) + 4H^+(aq) + O_2(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l) \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \tag{4}$$

Reaction conditions such as redox, adsorption (Kanel et al., 2005; Giasuddin et al., 2007) and co-precipitation (Fu et al., 2013) are the main mechanisms of contaminant removal following the application of nZVI. Issues that could also be a concern during application of nZVI for contaminant treatment are the technical challenges requiring evaluation of the design, operation and the radius of influence. In addition, there is a possibility that intermediate products could be produced even when contaminant disappeared following the treatment technology.

1.5.1. Catalytic role in persulfate oxidation

In-situ chemical oxidation (ISCO) is a cost effective environmental remediation technology involving reactive chemical oxidants to mineralize range of contaminants in soil and groundwater through non-specific chemical oxidation process (Watts and Teel, 2006; Huling and Pivetz, 2006; Crimi and Siegrist, 2005; Tsitonaki et al., 2010; Wang et al., 2013a; Zhao et al., 2013b). The common oxidants used in the ISCO treatments are hydrogen peroxide (H_2O_2), permanganate (MnO_4^-), persulfate ($S_2O_8^{2-}$), and ozone (O_3). For successful treatment efficiency, the selection and optimization of oxidants and catalysts is important.

In recent years, the treatment of some organic pollutants using persulfate oxidation chemistry has gained importance (Tsitonaki et al., 2010; Liang et al., 2008b, 2008c; Usman et al.,

Fig. 3 – Capping nZVI with poly acrylic acid (PAA).

2012; Zhao et al., 2013b; Fang et al., 2013; Zhou et al., 2013; Yang et al., 2011; Roshani and Karpel Vel Leitner, 2011). Several reports showed the catalytic role of nZVI used for the degradation of environmental contaminants such as chlorinated organics (Liu et al., 2005; El-Temsah and Joner, 2013; Liu and Zhang, 2010), nitrites (Liang et al., 2008d) and heavy metals (Ponder et al., 2000; Giasuddin et al., 2007). Persulfate is stable and through the activation of the oxidant under various conditions generates a strong aqueous oxidizing species, sulfate free radical ($SO_4^{-\cdot}$), with a redox potential of 2.6 V. Its high solubility, fast kinetics and stability which can be transported greater distances in subsurface and operation over a wide pH range are advantages over the peroxide (Fang et al., 2013; Adewuyi and Sakyi, 2013; Block et al., 2004). In addition to the oxidizing strength, persulfate has low affinity for soil organics (Block et al., 2004).

Reports showed the substantial treatment effect of the persulfate oxidation to remediate various contaminants such as oil hydrocarbon (Usman et al., 2012; Yen et al., 2011), polycyclic aromatic hydrocarbon (PAH) (Nadim et al., 2006; Zhao et al., 2013), methyl tert-butyl ether (Huang et al., 2002; Huling et al., 2011), TCE (Liang et al., 2004, 2008c), Polyvinyl alcohol (Oh et al., 2009), pharmaceuticals (Rao et al., 2014), Bisphenol A (Olmez-Hanci et al., 2013), benzene, toluene, ethylbenzene, and xylene (Liang et al., 2008a; Huang et al., 2005). Activators such as heat, UV light, and transition metals (such as Fe^{2+}) are commonly used to accelerate the oxidation rates of contaminants (Oh et al., 2009). Ferrous activated persulfate oxidation results in the rapid production of sulfate free radicals (see Eq. (5)).

$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-} \tag{5}$$
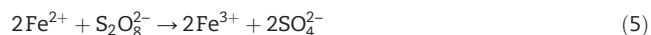
Persulfate oxidation of various organic contaminants using ZVI activation has been studied (Oh et al., 2009; Liang and Lai, 2008; Liang et al., 2008c; Le et al., 2011). As in the reaction equation delineated below (Eq. (6)), ZVI releases ferrous ion (Fe^{2+}) through corrosion which then facilitates the formation of the sulfate free radical (Oh et al., 2009; Liang et al., 2004; Lee et al., 2010; Anipsitakis and Dionysiou, 2004). Various reaction mechanisms are proposed in the activation of persulfate using ZVI (Al-Shamsi and Thomson, 2013; Liang and Lai, 2008) and the activation through direct release of Fe^{2+} following interaction with persulfate is assumed to be a promising approach in remediation (Liang and Guo, 2010). However, it is a concern that treatment efficiency could be limited as the higher dose of ZVI result in the conversion of the ferrous ion (Fe^{2+}) to ferric ion (Fe^{3+}) and with excess Fe^{2+}, a faster rate of radical scavenging may occur (Hussain et al., 2014; Liang et al., 2009). Through the application of organic chelating agent such as ethylenediaminetetra-acetic acid (EDTA) (Kwan and Chu, 2007; Liang et al., 2009), formate, malelate, citric acid, *etc.* in the iron, the contaminant removal efficiency has been improved. For example, Liang et al. (2009) examined the degradation efficiency of TCE in aqueous phase using EDTA chelated Fe^{3+} and demonstrated a faster persulfate activation.

$$Fe^0 + 1.5S_2O_8^{2-} \rightarrow Fe^{3+} + 3SO_4^{2-} \tag{6}$$
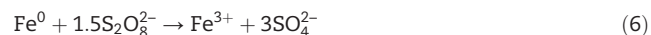
In recent studies, the nZVI catalyzed persulfate oxidation of organic contaminants showed promising result (Al-Shamsi

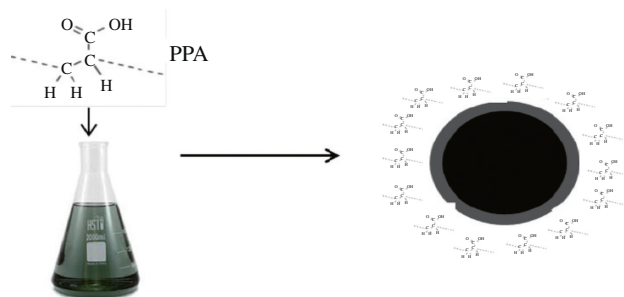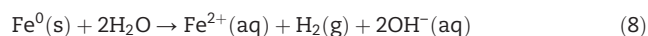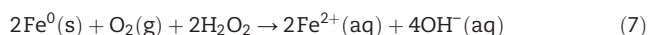and Thomson, 2013). The study reported nZVI as a favorable activator compared to the granular form due to its convenience in subsurface application. NZVI surface passivation resulted in a considerably reduced rate of TCE degradation following the first 45 min of treatment.

Studies in the use of nanocatalysts are crucial to the development of effective remediation approaches. The science and application of nanocatalysts is still in its infancy. The nano-sized particles present new opportunities for promoting, enhancing and controlling chemical activity, specificity, and selectivity. These unique catalytic properties have been achieved by the quantum size effects, composition, morphology and charge state of the catalysts. Moreover, due to the low mass-transfer limitations, the application of nanoparticles in advanced oxidation has more advantage of high reaction rates, short treatment times, capability of oxidizing contaminants in ppb level and avoids the need for catalyst recovery following the treatment. Development of nanocatalysts that can accelerate chemical oxidation without requiring UV radiation seems promising for environmental application, particularly for in situ remediation of subsoil and sediment contaminated sites (Liu et al., 2005).

1.5.2. Reductive technologies

One of the most widely used applications of zero-valent iron in environmental industries is its viability in the reduction process. The reaction of zero-valent iron with dissolved oxygen and water generates Fe(II) (Eqs. (7) and (8)) where released electrons become available to reduce contaminants (Keane, 2010). Further reaction of Fe(II) will form corrosion products such as Fe(III) hydroxides (Fe(OH)$_3$) and ferric oxyhydroxides (FeO(OH)) with high surface area which can immobilize pollutants (Manning et al., 2006; Kanel et al., 2005). This method has been extensively investigated and revealed its success in remediating contaminants which are sensitive to redox activity (Wilkin et al., 2005; Suzuki et al., 2012; Hwang et al., 2011; Agrawal and Tratnyek, 1995; Mu et al., 2004).

$$2Fe^0(s) + O_2(g) + 2H_2O_2 \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq) \qquad (7)$$

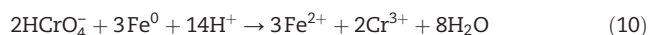$$Fe^0(s) + 2H_2O \rightarrow Fe^{2+}(aq) + H_2(g) + 2OH^-(aq) \qquad (8)$$

For example, for the degradation of chlorinated organic contaminants, such as TCE, chlorobenzene, dichlorodiphenyltrichloroethane (DDT), two known reaction pathways, i.e.,reductive and oxidative dechlorination, are suggested. Reduction of these compounds can be achieved either through direct reduction at the metal surface or reduction by ferrous iron or reduction by hydrogen with catalysis (Eq. (9)). The reduction potential of ZVI and dissolved ferrous iron is –0.440 V (Zhang and Elliott, 2006). The reactions of Fe^0 with TCE may be more complicated involving the release of electrons and the transformation of Fe^0 to ethane (Eq. (9)).

$$RCl + H^+ + Fe^0 \rightarrow RH + Fe^{2+} + Cl^- \qquad (9)$$

Chromium (Cr) is a reducible contaminant mostly present in industrial sites and military facilities, where its release into groundwater and soil has raised serious human and ecological health concerns due to its carcinogenic nature (Manning

et al., 2006). Chromium(VI) is listed as one of the major contaminants on the Superfund Priority List of Hazardous Substances for this very reason (Barnhart, 1997; Pellerin and Booker, 2000). The widespread use of chromium in the production of stainless steel, metal plating, pigment production and tanning of leather has led to the release of large quantities of Cr compounds into nearby soil and groundwater. In natural water, it exists in its oxidation state as chromium(VI) which is highly soluble and chromium(III) which has low solubility. Thus, the reduction of chromium(VI) in the toxic form to chromium(III) in the less toxic form is a potential treatment approach for soil and groundwater contaminated sites.

The use of ZNI has long been investigated and recognized for its ability to immobilize chromium(VI) using a permeable reactive barrier (Blowes et al., 1997; Puls et al., 1999; Astrup et al., 2000). Several bench-scale studies demonstrated the successful reduction of chromium using ZNI (Wilkin et al., 2005; Ponder et al., 2000; Lai and Lo, 2008; Gheju, 2011). In the reduction of Cr(VI) to Cr(III), Fe(0) is oxidized to Fe(II) and Fe(III) subsequently with precipitation of a sparingly soluble product, chromium(III)/iron(III) oxy-hydroxides, i.e., via direct (Eq. (10)) and indirect (Eq. (11)) reduction of Cr (VI) by Fe^0 and Fe(II), respectively (Chrysochoou et al., 2012).

$$2HCrO_4^- + 3Fe^0 + 14H^+ \rightarrow 3Fe^{2+} + 2Cr^{3+} + 8H_2O \qquad (10)$$

$$3Fe^{2+} + CrO_4^{2-} + 16H^+ \rightarrow 3Fe^{3+} + Cr^{3+} + 8H_2O \qquad (11)$$

2. Fate and toxicology

Given the versatile applicability, the ecological significance of nZVI appears inevitable due to the dramatic increase in production and use for environmental remediation (Grieger et al., 2010). Knowledge on the fate of these particles in the environment is limited. Depending on the particle size, the mobility, reactivity and persistence of these particles in environmental media vary. During the last few years, great public concerns have been raised on environmental and public health issues related to the application of nanomaterials. Therefore, toxicological studies investigating of the impacts of nZVI on ecology are increasing (Stern and McNeil, 2008; Kica and Bowman, 2013; Grieger et al., 2010). Moreover, contrary to the colloidal form of the same material, there is a need to understand the molecular or atomic level behavior in the context of contaminant remediation and their biological activity. More importantly, the change in conformation, through surface modifications, could alter the toxic effect of the particle due to a change in reactivity, size, sorption, and dissolution behavior. Toxicity studies considering both the bare and stabilized forms of nZVI could be timely, given that ecological risks identified are minimized through modification or with substitution of approaches in the synthesis, development and environmental application of the nanoparticles before succeeding to volume production. This section has a focus on the environmental behavior and toxicological implications of the bare nZVI and surface modified particles used for environmental applications.

Understanding the nature of interaction between nZVI particle and organisms and its effect on various level of biological organization is important. Two mechanisms are proposed, suggesting that nZNI can cause some toxic effect to ecological organisms. Direct interaction between nanoparticle and cell through binding to surface ligands is a possible mechanism which could involve large numbers of forces and molecular interactions; whereby the damage to cell membranes or the increased membrane permeability leads to leakage of cytosolic contents and cell death (Fig. 5) (Auffan et al., 2008; Li et al., 2010; Ševců et al., 2009). Surface properties of nZVI affected by various environmental conditions influence the type of interaction with the cell surface, which might be attributable to toxicological effect. Cellular interaction and the possibility of uptake by cell could be facilitated through the characteristic properties of the surface such as the surface charge, hydrophobicity and roughness of nZVI particle. The interaction of the surface charge of the particle with negatively charged phospholipid head groups or protein domains on cell surfaces is an important mechanism in the nano-bio interface causing deformation of membrane and internalization of particles (Nel et al., 2006; Fleck and Netz, 2004). Therefore, coating nZVI with anionic polymers such as poly(aspartic acid) could protect cell due to the electrosteric repulsion or less exertion of effect (Nel et al., 2006). (See Fig. 4.)

There have been few reports on the effect of nZVI to aquatic and soil organisms. Lee et al. (2008) examined the toxic effect of nZVI on *Escherichia coli*. From the study, strong bactericidal effect of the particle under aerated conditions and with notable physical disruption of the cell membranes was noticed. Production of various reactive oxygen species (ROS) resulting in lipid peroxidation, or oxidation of intracellular thiols and proteins and DNA were the mechanisms suggested. Through a two-electron transfer from the particle surface, some portion of the nZVI produces oxidants such as superoxide (O_2^-), H_2O_2, ferryl ion or were converted to $\cdot OH$. As a result of the oxidation or reduction process, the crystalline nature of the surface of particle may change. For example, following remediation of Cr(VI) by nZVI, treated samples exhibited the production of iron oxides, Cr–Fe (oxy) hydroxide and/or nZVI (Qiu et al., 2013; Li et al., 2008). Using molecular approach and utilizing treatment related biomarkers, the impact of nZVI to indigenous microbes was assessed. The study reported the change in the structure and composition of the soil bacteria population while no change in the expression ratios of the genes was observed.

In addition, due to the runoff from field of application or groundwater seepage, there may be a substantial exposure of dissolved iron to organisms in freshwater streams and ponds. Studies examined the potential ecological risks of nZVI to freshwater and marine organisms. Low concentrations of nZVI showed toxicity to the freshwater planktons, suggesting the role of oxidation products (ferrous and ferric irons) released from the ZVI particles. Moreover, the Fe^{2+}/Fe^{3+} entering the cytoplasm could cause oxidative stress which can damage surrounding cells, leading to the release of their intracellular contents (Keller et al., 2012; Li et al., 2009; Lee et al., 2008), whereas surface interaction between the ZVI and the organisms resulting in localized damage is reported (Keller et al., 2012).

Toxicity study investigating the effect of nano iron to medaka embryos at 48 hr of post-fertilization showed a dose-dependent decrease of superoxide dismutase (SOD) and increased level of malondialdehyde, while no terminal oxidative damage was observed during the whole exposure period, suggesting a chance of recovery (Li et al., 2009). The impact of nZVI to medaka fish through deposition of particles, swelling of cells and loss of scales was significant (Li et al., 2009), and nZVI exhibited changes in enzymatic activity of their embryos as a result of the ROS. Morphological change in gill rakers with disappearance of micro ridges in the taste buds was observed. Largely, it is established that the toxic effect of nZVI could be through the attachment and undesirable interaction of particles to cells and/or from the dissolved Fe^{2+} and Fe^{3+}. Findings from a recent study investigating the effect of nZVI on three coastal marine organisms such as mussel, sea squirt and urchin, showed a decrease in fertilization success of exposed sperm with further effect on embryo development (Kadar et al., 2013).

A phytotoxicity test exposing two plant species, *i.e.*, cattail (*Typha latifolia*) and hybrid poplars (*Populous deltoids × Populous nigra*), to different concentrations of nZVI was carried out. Following four weeks of treatment, nZVI exhibited a strong toxic effect on Typha at higher concentrations, while enhanced plant growth was observed at lower concentrations. Irregular aggregates of the nZVI were noticed on plant root surface where differing internalization of nZVI was observed for the root cells of the two species (Ma et al., 2013).

2.1. Aging affecting toxicity

As a result of the reactive nature, there is a significant relation between time and the structure and chemical properties of nZVI (Yan et al., 2013). Following exposure to water, the reactivity of nZVI in the first few days will be higher, however, the reactivity will reduce slowly over time (Tratnyek et al., 2014; Sarathy et al., 2008). Therefore, aged nZVI particles will have a reduced redox activity compared to fresh form and presumably affect its intrinsic toxicity. Due to the severe depletion of nZVI and increasing oxidation to Fe^{3+} oxides, the oxide layer of nZVI may govern the overall activity of the particle which as a result may decrease agglomeration, sedimentation rate, and the potential biological effects (Reinsch et al., 2010; Phenrat et al., 2008a; Liu and Lowry, 2006; El-Temsah and Joner, 2013). Few studies documented
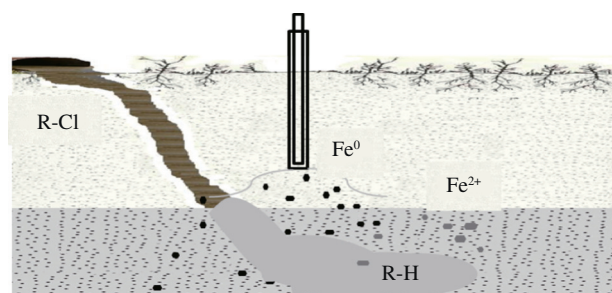

Fig. 4 – Reduction pathway of nZVI producing Fe^{2+} through contact with a contaminant. R-Cl: chloroalkanes; R-H: alkanes.
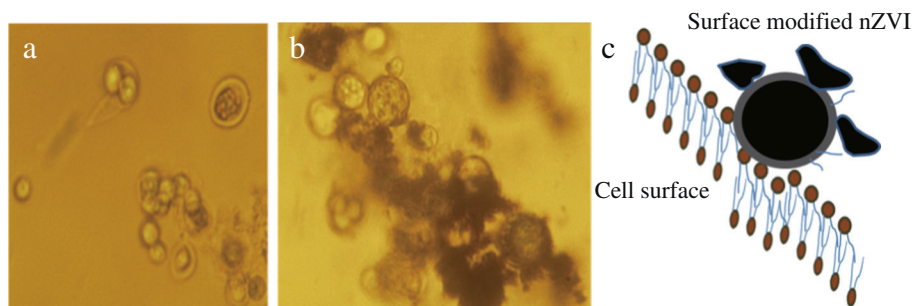
Fig. 5 – Microscopic image of interaction of cell to nZVI particles. (a) Untreated algal cell, (b) algal cell interaction with nZVI aggregates (shown in black), and (c) schematic drawing of interaction. nZVI: zero valent iron nanoparticles.

reduced toxic effect of aged nZVI (Li et al., 2010; Phenrat et al., 2008a). The formation of Fe-oxides on the particle surface was suggested in limiting adhesion to the cells by reducing sedimentation (Phenrat et al., 2008a; Li et al., 2010; Reinsch et al., 2010; El-Temsah and Joner, 2012). In real field application, the iron mineral phases present on the particle surface of nZVI will characterize the actual behavior in the environment. In one study, the toxic effect of fresh and aged (for one month) nZVI at concentrations of 500 mg/kg of soil to two species of earthworms, namely *Eisenia fetida* and *Lumbricus rubellus*, was reported. Significantly reduced toxic influence was observed in the aged nZVI treated samples (El-Temsah and Joner, 2012). Similarly, another study by El-Temsah and Joner ner, (2013) showed a reduced adverse effects of nZVI following oxidation.

2.2. Toxic influence of surface modifiers

Several toxicity studies are based on the bare nZVI, which is a potential assumption in dealing with the mode of action. However, in field applications, the stabilized form of nZVI is used to increase mobility into the underground aquifers (Li et al., 2010). Chemical nature and the chemical to cell interaction are important conditions elucidating the toxicity of materials. Thus, surface modifications can be a concern in the manner the functional changes, and may affect physiochemical properties and bioactivity of nZVI. In addition, due to the enhanced mobility and long life time in the environmental system, understanding the cellular interaction, uptake and toxicity can be important. Few reports are available examining the role of stabilized nZVI in modifying toxicity.

The role of a stabilizing agent in enhancing or reducing toxic influence differs. For instance, Li et al. (2010) elucidated a higher mortality and oxidative stress response of *E. coli* following exposure to carboxymethyl cellulose (CMC)-stabilized nZVI (Chen et al., 2012). In the same study, the bioaccumulation of the uncoated nZVI was higher. Authors suggested that the rate of oral ingestion might be high due to the preying and food-pecking behaviors of fish which may feed upon the aggregated form of the iron NPs that appear like a food. Moreover, Chen et al. (2011b) also reported the toxic effect of CMC coated nZVI to medaka (*Oryzias latipes*) fish. Factors such as hypoxia, released Fe(II) and ROS-mediated oxidative damage, were assumed to be contributing to the mechanism of toxicity. Zero valent iron

nanoparticles didn't show deleterious effect on total bacterial abundance whereas increased bacterial population was observed in the culture exposed to nZVI coated with a biodegradable polyaspartate (Kirschling et al., 2010). Likewise, a microglia and neurons culture from rodent exposed to surface-modified with polyaspartate showed a decrease in toxicity as the reduced sedimentation limited particle exposure to the cells (Phenrat et al., 2008a). On the other hand, olefin maleic acid copolymer coating showed a beneficial effect (Li et al., 2010). The study indicated the enhancing effect of an olefin maleic acid copolymer coating on the expression of genes responsible for coding the reductive dechlorination activity of *Dehalococcoides* sp. whereas in the cultures exposed to bare nZVI, these genes were down regulated by hundred-folds.

2.3. Influence of geochemical environment

Physical and chemical heterogeneities of the environmental settings (such as the oxidation-reduction potential, pH, dissolved oxygen, concentrations of SO_4^{2-} and NO_3^-) within and down gradient of the nZVI injection sites have significant impacts on the fate, transport, solubility, aggregation, bioavailability and toxicity of nZVI within groundwater and soil (Johnson et al., 2008, 2013; Kouznetsova et al., 2007). Physicochemical parameters such as natural organic matter, pH, and hardness may have significance in toxicity. For example, pH can affect mobility of nZVI particles due to the acquired negative charge affecting absorption strength and agglomeration (Zhang and Elliott, 2006). Humic acid can modify the toxic effect of nZVI on bacteria due to surface modification and the formation of floccus surrounding the cell (Chen et al., 2011a).

A research group from the United States Environmental Protection Agency (USEPA) evaluated the effect of groundwater solutes and dissolved oxygen on the oxidation of bare nZVI. In the study, the particle was aged under various conditions where different anions showed varying passivation of the iron surface and progression of oxidation over time. In the same study, depending on the concentration and composition of anions, varying products were formed such as maghemite within the oxide layer, vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, and Fe–S minerals, *e.g.*, schwertmannite and pyrite. Yu et al. (2006) suggested that formation of vivianite might passivate surface of nZVI and may modify biological activity. While

application is considered to affect the treatment of contamination plume, the geochemical influence may give nZVI a chance of leaving the site and subsequently have a potential toxic influence to non-target environmental sites.

3. Cost of nZVI

Although nZVI has unique properties over the existing technologies due to high reactivity for contaminant removal, sufficient mobility and stability within soil, the cost of operation is essential due to the low market value for remediation technologies. Unlike the cost of bulk form of iron, iron nanoparticles are expensive because of the high production cost. Given the limited number of suppliers available, the cost of nZVI in 2001 was as high as 500 USD/kg. Between 2004 and 2006, the price for nZVI was within 100-folds of the price of micro and granular forms of ZVI; however the nZVI were having improved effectiveness due to the improved particle characterization techniques and gained an increased number of suppliers, and as a consequence, made its use in remediation market viable.

4. Conclusions and future research perspectives

Nano-scale zero valent iron (nZVI)-based technologies are valuable technologies for environmental remediation. The limited mobility of bare nZVI might have minimal effect on remediate contaminated sites. The detrimental effect of nZVI to water and soil organisms was reviewed. However, such studies have a limit as the actual toxic effect reported so far is not necessarily caused by the primary size of nZVI due to the aggregation of particles. While a stabilized form of nZVI has the advantage over bare form due to the improved efficiency and reduced toxic influences, consideration of coating agent based on its life time is important to protect the introduction of additional contamination load to the site. The review indicated that anionic polymers were protective due to less exertion of effect on cell. No sufficient information was available on the long term exposure to lower concentrations of nZVI obtaining chronic end points. An important development in synthesizing nZVI is the technique that makes use of biological route. From the perspective of the reviewed literatures, studies emphasizing on the following areas will be essential, *i.e.*, examining the toxic effect of intermediate reaction products. It is worthwhile to consider customization of coatings to a particular environmental system while reducing the toxic influence of nZVI to the ecology.

Understanding nZVI particle to cell interaction is important. Robust approach for a cost effective and large scale production of nZVI is important.

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